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Small-Scale Pilot Evaluation of Calcium- and Sodium-Based Sorbents for Dry SO2 Removal

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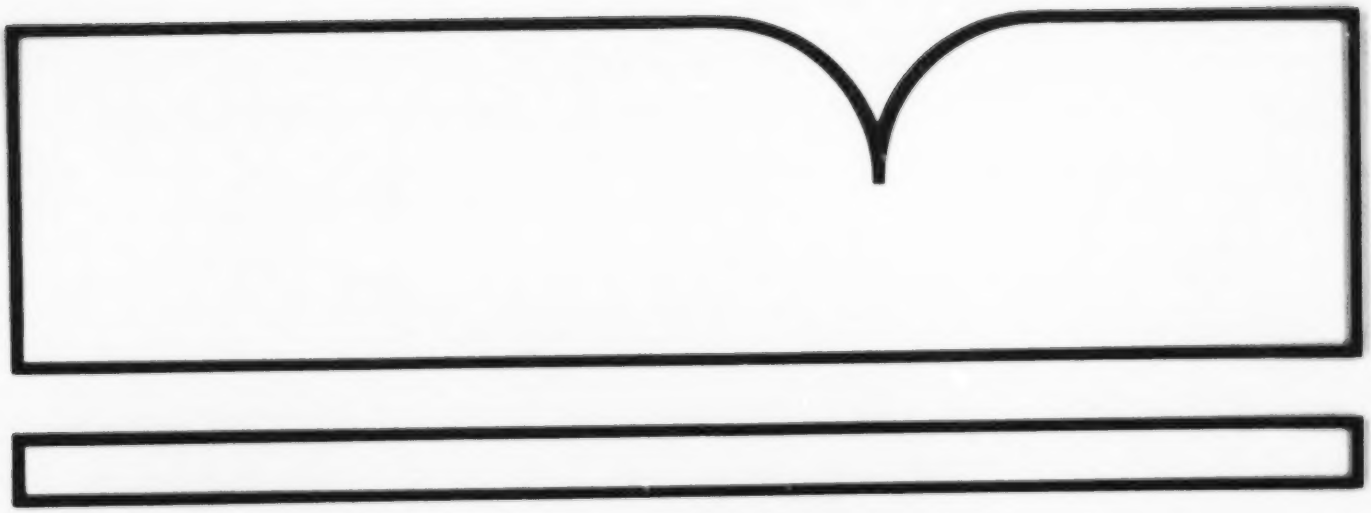

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SMALL-SCALE PILOT EVALUATION OF CALCIUM- AND SODIUM-BASED SORBENTS FOR DRY SO_2 REMOVAL

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16. ABSTRACT The paper discusses a 100 cu m/h pilot facility (consisting of a spray dryer, a sorbent injection system, a duct section, and a pulse-jet baghouse or cyclone separator) used for testing the reaction at low temperature between various calcium- and sodium-based sorbents and SO2 in the concentration range of 1000-2500 ppm. The sorbents tested were based on earlier-reported sand-bed reactor (0.3 cu m/h) tests. The performance of these sorbents is compared in terms of SO2 removal and stoichiometry with that obtained using conventional slaked lime in spray drying or dry injection under similar conditions.

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A 100 m^3/h pilot facility incorporating a spray dryer, a sorbent injection system, a duct section, and a pulse jet baghouse or cyclone separator was used for testing the reaction at low temperature between various calcium- and sodium-based sorbents and SO_2 in the concentration range of 1000-2500 ppm. The specific sorbents selected for testing were based on earlier reported sand-bed reactor (0.3 m^3/h) tests. The performance of these sorbents is compared in terms of SO_2 removal and stoichiometry with that obtained using conventional slaked lime in spray drying or dry injection at similar conditions.

INTRODUCTION

Recent research and development work in the area of dry flue gas desulfurization (FGD) seems to have concentrated on bench and small pilot plant testing (1-8). The emphasis of this work has been on studying the versatility of small-scale testing equipment in relation to full-scale facilities, as well as the development of new or innovative sorbents and processes. Reference 5 described a test program using a 100 m^3/h (50 cfm) mini-spray dryer/pulse jet baghouse facility for removal of sulfur dioxide (SO_2) from a simulated flue gas by spraying a slaked lime [$Ca(OH)_2$]/flyash slurry into the gas stream, similar to the conventional spray drying process in operation at several coal-fired power plants in the U.S. The mini-pilot plant work revealed that fairly good agreement could be reached between full-scale, large pilot, and mini-pilot plant performance with respect to SO_2 removal efficiency, stoichiometric ratio (SR), approach to saturation (Δt_s), and other SO_2 control system parameters.

The present work continues the concept of mini-pilot plant testing for the evaluation of sorbents and test parameters, following bench-scale screening tests in a sand-bed reactor [0.325 m^3/h (approx. 10 cfh)] which identified promising improvements for dry FGD. Whereas most earlier dry FGD work concentrated on the use of spray drying for the introduction of the alkaline sorbent as a slurry into the SO_2-laden flue gas, the present work emphasizes dry injection of sorbent into the humidified and/or temperature-controlled flue gas, simulating flue gas conditions between the air preheater and the particulate control device [fabric filter (FF) or electrostatic precipitator (ESP)] in a coal-fired power plant. Both calcium- and/or magnesium-based sorbents were used in this test series as well as

sodium bicarbonate. The test results are compared with previous bench- and pilot-scale results.

Reference 6 reported the bench-scale development of very reactive flyash-enhanced lime sorbents, while a recent paper (8) reported the continued effort to enhance lime using silica compounds via bench-scale as well as mini-pilot plant testing. The continuation of this work is reported here. However, most of the previous pilot plant work used a baghouse for the collection of particulate matter, while the present work also used a cyclone separator as the particulate control device downstream of the duct where sorbents were introduced. The duct/cyclone configuration simulates the short residence time of particulates in an ESP, and therefore is well suited to a preliminary study of a dry sorbent injection system for SO_2 removal which has been retrofitted to an existing power plant equipped with an ESP.

The work discussed here was performed for the U.S. Environmental Protection Agency at AEERL's in-house facilities in Research Triangle Park, North Carolina.

APPARATUS

The pilot plant facility shown in Figure 1 consists of: a Niro Atomizer spray dryer, providing a gas retention time of about 10 seconds and equipped with a rotary atomizer for atomization of water or slurry; an electrical air heater and an SO_2 injection system, located upstream of the spray dryer; a dry sorbent injection system following the spray dryer vessel; a heat-traced and insulated 5-cm (2-in.) diameter duct section 9.8 m (32 ft) in length [alternatively 24.4 m (80 ft)], providing a gas retention time of 0.8 s (alternatively 2.0 s); a pulse jet baghouse with four polyester bags, providing a total solids collection area of 2.3 m^2 (25 ft^2); an induced draft fan;

and a stack for exhausting the cleaned flue gas into the atmosphere. Alternatively, a cyclone separator with a cut size of about 3 μm can be inserted just upstream of the baghouse to collect a large fraction (normally 80-95 percent) of the particulate. The normal gas flow in this facility is 68 m^3/h at 20°C (68°F) or 40 dscfm. SO_2 is injected at a rate of 0.18-0.45 kg/h (0.4-1.0 lb/h) into the heated air to provide an SO_2 concentration of 2.67-6.67 g/m^3 (1000-2500 ppm) at 20°C (68°F).

In most of the present work, water only was fed through the rotary atomizer to simulate water vapor in a humidified flue gas [adiabatic saturation temperature was around 40°C (104°F)], and the dry sorbent was injected into the vertical duct downstream of the spray dryer by a solids feeder (Vibra Screw or AccuRate volumetric feeder). In some of the initial work, however, the sorbent was introduced as a slurry by the rotary atomizer and dried in the spray dryer. The sorbents were entrained with the flue gas throughout the duct and discharged batchwise from the baghouse hopper. The baghouse was normally operated with a pressure drop of 50-100 mm (2-4 in.) WG. In some tests, however, the pressure drop was lower, 25-50 mm (1-2 in.) WG. The solids were discharged continuously from the system into a bucket when using the cyclone separator for particulate collection (the gas leaving the cyclone passed through the baghouse prior to its exhaust into the atmosphere).

The electrical heater normally raised the temperature of the simulated flue gas to 177°C (350°F) prior to humidification by evaporative cooling to the range of 49-93°C (120-200°F) in the spray dryer. The approach to saturation at the spray dryer outlet (Δt_a) was closely controlled using comparisons between the dry and wet bulb

temperatures. The gas temperature was monitored by thermocouples throughout the system, verifying that the heat tracing and insulation maintain constant temperature in the duct section, although the temperature drop across the baghouse was from 1 to 3°C (2 to 5°F) due to heat loss. The SO_2 injection rate was monitored using a calibrated rotometer, and the injection rate of sorbent was determined using the weighing-stopwatch method. The SO_2 concentrations throughout the system were determined by extractive sampling normally from the spray dryer inlet duct, the spray dryer outlet duct/cyclone outlet duct/baghouse inlet duct, and the baghouse outlet duct, and analyzed by continuous monitors (an Anacon model 207 non-dispersive ultraviolet spectrophotometer and a Thermo Electron model 40 pulsed fluorescent analyzer have been used). Data (temperatures, pressure drops, flows, SO_2 concentrations) are normally collected every half-hour during a 4-8 hour test run at fairly constant conditions.

INITIAL SPRAY DRYING AND DRY INJECTION TESTING

Spray Drying of Calcitic and Dolomitic Hydrated Lime

The initial testing done on the mini-pilot plant used spray drying of a lime slurry. Problems with pluggage of the four wheel inserts, similar to those reported by others (5), were reduced significantly by mixing flyash (Appalachian Power Co., Clinch River Plant—low calcium flyash) with lime slurry to increase the total solids content to about 30 percent in the slurry. The flyash is believed to reduce the potential for plugging in the wheel both by lowering the sedimentation rate of the slurry as well as providing sufficient abrasive material to erode any solids buildup that might occur in the inserts.

Most tests were done using an approach to saturation of 14-17°C (25-30°F). Little product deposition was observed on the spray dryer

walls. The dry solids were entrained by the gas throughout the 0.8 s gas retention time duct section and deposited on the bags, allowing the pressure drop to reach a steady value of 25-50 mm (1-2 in.) WG. This pressure drop range corresponded to a bag cleaning frequency of 10-15 min.

Both calcitic and dolomitic hydrated limes were tested. The stoichiometric ratio (SR) for the system is defined as:

$$SR = \frac{\text{mol/h of } Ca(OH)_2\text{* injected}}{\text{mol/h of } SO_2 \text{ injected}} \quad (1)$$

(*plus $Mg(OH)_2$, if applicable)

In this test series, the SR ranged from 0.8 to 2.5.

Tests were made at SO_2 inlet concentration levels of 1000, 1500, and 2500 ppm during each test, and the SO_2 outlet concentration of the system was measured. The SO_2 removal across the system is defined as:

$$SO_2 \text{ removal} = \frac{\text{mol/h } SO_2 \text{ in} - \text{mol/h } SO_2 \text{ out}}{\text{mol/h } SO_2 \text{ in}} = \frac{\text{mol/h } SO_2 \text{ removed}}{\text{mol/h } SO_2 \text{ in}} \quad (2)$$

The SO_2 removal results are depicted in Figure 2. As expected, the SO_2 removal efficiency increases with increasing SR for all SO_2 concentration levels. Also, for a given SR, the highest SO_2 removal efficiency was achieved at the lowest concentration level, as seen by comparing the 1000 and 2500 ppm test series. For the SO_2 inlet concentration of 2500 ppm, less than 90 percent SO_2 removal was obtained even with an SR around 2.5. About 95 percent removal was achieved at this SR at an inlet concentration of 1000 ppm SO_2. These results agree well with previously reported spray drying absorption test results.

If the concept of sorbent utilization is defined as

$$\text{Utilization} = \frac{\text{mol/h } SO_2 \text{ removed}}{\text{mol/h } Ca(OH)_2{}^* \text{ injected}} = \frac{SO_2 \text{ removal}}{SR} \qquad (3)$$

(*plus $Mg(OH)_2$, if applicable)

this definition, via the right-hand expression, shows that in the spray drying system sorbent utilization decreases with an increase in SO_2 inlet concentration for a given SR. Earlier bench-scale testing (4) showed that the same overall conversion of $Ca(OH)_2$ [plus $Mg(OH)_2$, if applicable] was achieved for various SO_2 inlet concentrations after 1 h exposure of $Ca(OH)_2$ in the sand-bed reactor. It therefore appears that the lower utilization of $Ca(OH)_2$, which was achieved at the higher SO_2 inlet concentration levels in the pilot plant (as compared to the lower SO_2 inlet concentrations), reflects the much shorter exposure time of the sorbent to flue gas in the spray dryer/baghouse pilot plant. A longer sorbent residence time in the baghouse and/or the introduction of sorbent recycle is therefore the logical way to improve the flue gas/sorbent mixing and especially to increase SO_2 removal at high SO_2 concentrations.

The short test series performed using pressure-hydrated dolomitic lime as sorbent revealed no clear improvement in SO_2 removal efficiency or sorbent utilization relative to the calcitic lime at high sulfur concentrations (2500 ppm SO_2). This finding agrees with earlier bench-scale test studies (4), where no improvement in sorbent conversion could be observed when comparing results using pressure-hydrated dolomitic limes with those obtained using reagent grade $Ca(OH)_2$.

Dry Injection of Hydrated Lime

A test series was undertaken using hydrated lime as a dry injection sorbent for SO_2 removal. The heated air stream containing 1500-2500 ppm SO_2 was humidified to an approach to saturation (Δt_s) of 11-17°C (20-30°F) by water evaporation in the spray dryer. Hydrated lime was injected to provide an SR in the range of 1.7-3.3 downstream of the spray dryer and entrained by the gas to the baghouse for collection [baghouse pressure drop of 25-50 mm (1-2 in.) WG]. While the detailed results from this test series have been reported and discussed elsewhere (8), Figure 3 shows the measured SO_2 removal efficiency as a function of SR. It appears that even the use of an SR of 3 results in an SO_2 removal of no more than 30-40 percent, which is significantly lower than what was reported above using spray drying absorption (i.e., introducing the $Ca(OH)_2$ as a slurry) at similar conditions of outlet temperature and humidity. These results indicate that dry injection of hydrated lime downstream of the humidification vessel normally would be a fairly inefficient process for SO_2 removal compared with lime spray drying.

Dry Injection of Sodium Bicarbonate

Sodium bicarbonate ($NaHCO_3$) has traditionally been tested and recommended as a dry injection sorbent for SO_2 removal at relatively high flue gas temperatures [i.e., approx. 120-180°C (250-360°F)], as the decomposition of $NaHCO_3$ to sodium carbonate (Na_2CO_3) at these temperatures is believed to favor its reaction with SO_2. Previous sand-bed reactor tests (4), however, demonstrated that dry $NaHCO_3$ also was very reactive with SO_2 at lower temperature [64°C (148°F)] and higher relative humidities (30-75 percent).

A small test series was performed using dry injection of a commercial sodium bicarbonate, Church and Dwight regular Grade 1, into the simulated flue gas containing 2500 ppm SO_2 at four temperatures in the range 49-138°C (120-280°F). The rotary atomizer was used for water evaporation via flue gas cooling to simulate the flue gas moisture contents in the low temperature range (supplemented with evaporative flue gas cooling). The sorbent was entrained with the simulated flue gas througout the 0.8 s retention time duct to the baghouse for collection. The test conditions and results are shown in Table 1. As two mols of $NaHCO_3$ are expected to react per mol of SO_2 removed, a "normalized stoichiometric ratio" (NSR) is defined here in agreement with previous usage as:

$$NSR = \frac{2 \times (\text{mol/h of } NaHCO_3 \text{ injected})}{\text{mol/h of } SO_2 \text{ injected}} \qquad (4)$$

All tests were run using an NSR in the range of 1.9-2.5. It appears from the data in Table 1 that the SO_2 removal efficiency for a given SO_2 inlet concentration decreases with decreasing temperature at the point of sorbent injection. This efficiency decrease may be more appropriately correlated with the lower temperature in the baghouse (where most of the reaction is believed to take place) as a very significant heat loss occurs in the baghouse at the high temperatures. The two tests performed (Table 1) at low temperature [49°C (120°F)] and high relative humidity [60 percent, corresponding to a Δt_s of 10°C (18°F)] revealed an increase in utilization from 18 to 31 percent when the SO_2 inlet concentration was lowered from 2500 to 1500 ppm; however, these data do not seem to agree with earlier bench-scale studies (4). The bench-scale results generally indicated higher conversions than the corresponding sorbent utilizations observed in this pilot plant test

series. It is believed that this can be explained by the fairly coarse particle size (50–60 μm) of the sorbent used which caused most of the product to deposit in the baghouse hopper. The consequent low sorbent deposition on the fabric filter bags resulted in insufficient contact between the SO_2-laden flue gas and the solids [this effect has also been reported by others (5)]. The relatively low pressure drop observed during these tests [15–50 mm (0.6–2 in.) WG] supports this theory.

A specially fine ground $NaHCO_3$ from the same supplier with a mean particle size less than 10 μm was used in a second test series and resulted in a markedly increased SO_2 removal efficiency. An increased pressure drop across the baghouse [50–100 mm (2–4 in.) WG] also reflected an increased product deposition on the bags. The SO_2 removal efficiency obtained in these tests (Figure 4) reveals an SO_2 removal increasing from 54 to 97 percent when the NSR is increased from 0.6 to 1.4. This corresponds to a sorbent utilization of 70 percent and higher at a baghouse outlet temperature of 82°C (180°F). Also, note that an increase in the SO_2 inlet concentration did not adversely impact the overall SO_2 removal efficiency (or sorbent utilization), which is in agreement with the earlier mentioned bench-scale work (4).

Two tests were performed injecting the fine-grind product at fairly low NSR (0.3 and 0.5) into the simulated flue gas at low temperature [49°C (120°F)] and high relative humidity (60 percent). Very high SO_2 removal efficiency was obtained (43 and 72 percent, respectively), as also shown in Figure 4. This indicates that more than the "normal stoichiometric" amount of SO_2 reacted with the sorbent. A possible explanation of this phenomenon is that only one mol of $NaHCO_3$ reacted per mol of SO_2 at these conditions, so that the

product of reaction was sodium bisulfite ($NaHSO_3$) rather than sodium sulfite (Na_2SO_3). This reaction could occur if little or no thermal decomposition of $NaHCO_3$ took place at low temperature and high relative humidity. This proposed mechanism is not inconsistent with the earlier sand-bed reactor test results (4). Assuming this mechanism at low temperature and high relative humidity, the definition of stoichiometric ratio should consequently be changed to:

$$NSR^1 = \frac{\text{mol/h of } NaHCO_3 \text{ injected}}{\text{mol/h of } SO_2 \text{ injected}} \qquad (5)$$

The use of this definition has been indicated by the arrows in Figure 4 for the tests performed at low temperature [49°C (120°F)]. It is interesting to note that the sorbent utilization which can be calculated using NSR^1 is of the same order of magnitude as that seen at the higher temperature [82°C (180°F)] when using the conventional definition of NSR.

DRY INJECTION TESTING USING SILICA-ENHANCED LIME SORBENTS

Previous Bench-Scale Testing

Previous bench-scale studies (6-8) have demonstrated that slurrying of silica (SiO_2)-containing compounds (such as flyash and diatomaceous earth) with lime at favorable time/temperature conditions can enhance the subsequent dry conversion of $Ca(OH)_2$ with SO_2 in a sand-bed reactor, as compared to the conversion of pure $Ca(OH)_2$. The main reason for this silica enhancement of $Ca(OH)_2$ with respect to the dry reaction with SO_2 is believed to be related to the pozzolanic reactions occurring in the silica-lime-water system. The rates of these reactions increase with slurrying temperature and possibly also by the use of certain additives [such as sodium hydroxide (NaOH) and

sodium biphosphate (Na_2HPO_4)] that might promote the dissolution rate of silica via an increased slurry pH. Bench-scale studies indicated that the optimum enhancement of lime with respect to SO_2 removal occurred at a mol ratio of 1:1 between silica (from diatomaceous earth) and lime. This resulted in about 90 percent conversion of $Ca(OH)_2$ with SO_2 in the sand-bed reactor after a 1 h exposure at 64°C (148°F) and 60 percent relative humidity [Δt_s = 10°C (18°F)]. Differential scanning calorimetry has inferred the formation of a "new phase," identified as calcium silicate hydrate, by the reaction between SiO_2 and $Ca(OH)_2$ which is believed to be essential to the improved reactivity with SO_2. Bench-scale experiments using flyash as a source of SiO_2 also showed that increasing the total amount of flyash slurried with the lime significantly increased the enhancement effect with respect to SO_2 removal and/or reduced the time required for reaching optimum enhancement.

Pilot Plant Tests Using Duct Injection/Baghouse System

Mini-pilot plant testing was performed using dry injection of the above-discussed silica-enhanced lime sorbents into the flue gas duct (providing a gas residence time of 0.8 s) followed by a baghouse for particulate collection. These pilot plant test results confirmed the significant enhancement by silica of $Ca(OH)_2$ as a dry sorbent for SO_2 removal (8). As a background for the work to be discussed here, these tests (8) are summarized as:

1) Lime and the silica source were slurried at normally 15-30 percent solids and stirred in a heated [85-95°C (180-200°F)] tank for 12-16 h.
2) The "reacted" slurry revealed very difficult drying characteristics; i.e., it could not be easily spray dried at

the low approach to saturation [Δt_s of 10-70°C (18-130°F)] normally used in FGD and acid gas control systems. Filtration of the slurry to a 50-60 percent moisture cake followed by oven drying, however, produced a dry (less than 5 percent residual moisture) product which could easily be crushed into a fine, free-flowing powder suitable for dry injection.

3) The dry sorbent prepared as described above was injected into the humidified, simulated flue gas, and the SO_2 removal across the system was measured for an SR [with respect to $Ca(OH)_2$] range of 0.8-2.5. Figure 5 shows the results when using flyash as the silica source.

4) The results in Figure 5 show that a flyash-to-$Ca(OH)_2$ ratio of about 3:1 provides for optimum enhancement of $Ca(OH)_2$ with respect to dry SO_2 removal at the test conditions noted. Removal efficiencies of 50-90 percent were achieved for a lime stoichiometry in the range 1 to 2.5.

5) A lime utilization of 40-50 percent was achieved in the sorbent's "first pass" through the pilot plant at the given conditions, as shown in Figure 6 for the flyash-enhanced sorbent. Some selected "recycle" tests using the product in a "second pass" through the pilot plant indicated that the sorbent utilization could be increased to 60-80 percent (see Figure 6). These "dry recycle" data suggest that the key to a very high utilization of the enhanced sorbents lies in increasing their residence time in the gas stream.

Flyash would obviously be the most practical silica source at any coal-fired plant with an FGD installation. Slurrying flyash with quicklime at an elevated temperature appears plausible in, or just

downstream of, a conventional lime slaker operating at 85-95°C (180-200°F). The "reacted" slurry mixture could be dewatered and dried commercially as a continuous flash or fluid-bed drying of the filter cake, using a flue gas slipstream for drying and/or introducing the wet sorbent into the main flue gas stream.

An alternative or supplemental route for reducing the moisture content of the sorbent filter cake which was tested on the mini-pilot scale was the mixing of two parts (by weight) of dry recycle solids into one part of sorbent filter cake having 50-60 percent moisture. This produced a sorbent mixture with approximately 20 percent moisture. An important observation was that the produced sorbent mixture appeared sufficiently "dry" so that it could be handled in most conventional solids handling equipment. It was injected as a sorbent into the flue gas duct, resulting in its drying to about 5 percent residual moisture and a lowering of the flue gas temperature due to the moisture evaporation occurring simultaneously with SO_2 removal. This concept avoids any separate drying process for the freshly prepared sorbent. It also permits the continuous recycle of sorbent, which leads to higher utilization and lower lime consumption.

The initial series of consecutive recycle tests using the above concept of injecting a "moist" sorbent into the duct indicated very high overall lime utilizations; about 50 percent SO_2 removal was achieved for an overall SR of 0.5 at an approach to saturation of 11-17°C (20-30°F) at the baghouse outlet. An example of a more comprehensive recycle test series is shown in Table 2, using seven consecutive tests at an overall lime stoichiometry of about 0.6. It appears that the lime utilization decreased from an "apparent" value of 115 percent in the first recycle test (due to excess alkalinity from

the previous run) and leveled off at around 80 percent lime utilization later in the test series. Note that the approach to saturation, Δt_s, was about 10°C (18°F) and that a slight increase in temperature was observed across the baghouse as a result of the SO_2/sorbent reaction on the filter bags. Also, up to about 30 percent of the total SO_2 removal seemed to occur in the duct section prior to the baghouse.

Pilot Plant Tests Using Duct Injection/Cyclone Separator System

Mini-pilot plant testing was also performed using dry injection of the flyash-enhanced lime sorbents [flyash/$Ca(OH)_2$ weight ratio = 3:1] into the flue gas duct providing a gas retention time of 2.0 s and equipped with a cyclone separator downstream for collecting most of the particulates. Gas was sampled at the inlet to the system and immediately downstream of the cyclone to assess the SO_2 removal across the duct section/cyclone system. Testing involved a simulated flue gas containing 1500 ppm SO_2 and humidified to an approach to saturation (Δt_s) in the range of 5-16°C (9-28°F) just prior to the point of sorbent injection. A stoichiometric ratio (SR) in the range from 1 to 3 was used [based on $Ca(OH)_2$]. The sorbents tested were prepared by oven drying [for about 36 h at 85°C (185°F)] as well as by spray drying in a larger facility [approx. 2400 m^3/h at 20°C (68°F) or 1400 scfm] using a high spray dryer outlet temperature [115°C (240°F)].

The SO_2 removal results shown in Figure 7 indicate that 20-35 percent removal is achieved for an SR ranging from 1 to 3 and a Δt_s of about 11°C (20°F). Comparison of these results with those in Figure 5 reveals that this is about 50-33 percent of the SO_2 removal achieved when using the same sorbent at similar conditions but injecting it into the shorter gas retention time duct (0.8 s) equipped with a baghouse. The overall longer residence time of the sorbent in the gas stream

and/or more efficient contact between sorbent and flue gas in the baghouse system seems to explain the higher SO_2 removal achieved when using a baghouse rather than the cyclone. Note, however, that the above data also suggest that the approach to saturation (Δt_s) is the single most important parameter affecting the SO_2 removal across the duct section. This is best illustrated by the 50 percent removal achieved at a Δt_s of 5°C (90°F) versus only 9 percent removal obtained at a Δt_s of 16°C (28°F).

The results in Figure 7 also indicate that no SO_2 removal difference in the duct (2.0 s gas retention time) of the mini-pilot plant can be observed between the sorbent prepared by spray drying and that prepared by oven drying, despite the coarser particle size of the spray-dried product. It is believed, though, that the sorbent in the present test series was well dispersed in the gas stream throughout the duct section with no possibility for settling of the coarser sorbent fraction. This may be contrary to the baghouse situation, where the much lower gas velocity in the hopper provides for easy separation of the coarser particles from the gas stream (5).

The concept of sorbent recycle was introduced by mixing freshly prepared sorbent filter cake (about 60 percent residual moisture) with recycle solids in a solids mixer at a weight ratio of 1:2. The mixed product, although appearing "dry," had about 20 percent residual moisture and was injected into the simulated flue gas. This lowered the flue gas temperature due to moisture evaporation to an approach to saturation (Δt_s) of about 10°C (18°F) at the cyclone outlet and produced a dry product which was collected by the cyclone separator.

The SO_2 removal shown in Figure 8 for a series of consecutive test runs reveals that about 50 percent overall utilization of the lime was

obtained in the duct section by recycling the cyclone catch. The 1:2 mixing ratio used corresponds to a sorbent recycle ratio of 5:1 in terms of dry solids, meaning that the average residence time of the sorbent is increased from 2 to about 10 s. In addition to the increased sorbent residence time in the gas stream, however, the effect of used solids activated by re-mixing with wet sorbent might be an important factor also which cannot be separately evaluated by these data. Although the mechanism is not yet fully understood, the approximately 50 percent SO_2 removal at an SR of 1 in a duct/cyclone dry injection system clearly indicates the advantages of recycle.

The above tests were done using flyash only for the enhancement of lime (flyash/hydrated lime weight ratio = 3:1) by slurrying at elevated temperature, 85-95°C (180-200°F), for 12-16 h. Since flyash from a utility FGD system would not normally be collected separately from the dry FGD product, a test series was undertaken using the mixture of flyash and FGD products [calcium sulfite/sulfate ($CaSO_3/SO_4$) and unused lime] collected in previous tests for the enhancement of lime at elevated slurry temperature. Normally, a mixture of about 70 percent flyash, 20 percent $CaSO_3/SO_4 \cdot H_2O$, and 10 percent unused $Ca(OH)_2$ was sought. This represents the composition of the solids collected from an ESP downstream of a duct injection FGD system cleaning a flue gas containing 1500 ppm SO_2, and assumes that an SR of 1 would enable an SO_2 removal efficiency of 50 percent (using recycle mode). The recycle solids were slurried with $Ca(OH)_2$ at a weight ratio of 4.5:1 (corresponding to a flyash/$Ca(OH)_2$ ratio of 3:1) at 85-95°C (180-200°F) for 12-16 h. Additional recycle solids were later added to the produced sorbent, resulting in a product with 20-30 percent residual moisture and suitable for duct injection.

Consecutive tests were done at different sorbent injection rates (different SRs), and the SO_2 removal results are depicted in Figure 8. One conclusion from these tests is that the presence of FGD reaction products ($CaSO_3/SO_4$) during slurrying at elevated temperature did not seem to adversely impact the silica enhancement of lime. Also, 50-90 percent SO_2 removal was achieved in the duct injection/cyclone system with an SR in the range of 1 to 2, again reflecting a lime utilization of about 50 percent.

Two different procedures for adding additional recycle solids to the slurry of flyash-enhanced lime have been tested. The original concept used slurrying (lime enhancement) at 30-percent solids followed by filtration to produce an approximately 60-percent-residual-moisture filter cake, which (by adding two parts recycle solids per one part filter cake in a solids mixer) produced an approximately 20-percent-moisture material suitable for duct injection. Later, an alternative method used lime enhancement at a higher slurry solids content (about 35 percent) to which two parts of recycle solids per one part of slurry added in the solids mixer produced a material with around 25 percent moisture. This material was sufficiently dry for handling by conventional solids handling equipment; i.e., it could be used for duct injection. The second procedure, which avoids separate drying and filtration, seems to be the more attractive because of its simplicity and low equipment costs for a continuously operating large scale facility. A flow diagram illustrating this process is shown in Figure 9.

CONCLUSIONS

- The mini-pilot plant is an efficient and effective tool for studying dry FGD reactions in a continuous process mode, for

both spray dryer and dry sorbent injection studies.

- In-duct injection of dry $Ca(OH)_2$ into a humidified SO_2-laden flue gas stream results in significantly less SO_2 removal in the duct/baghouse or duct/cyclone system than in a lime spray drying system.
- In-duct injection of dry $NaHCO_3$ at low temperature [49-93°C (120-200°F)] and high relative humidity (up to 60 percent) results in very high SO_2 removal, if the injected sorbent has a particle size sufficiently small (less than 10 μm) to allow effective gas entrainment of the particles and their deposition on the fabric filter bags. At low temperature [49°C (120°F)], the thermal decomposition of $NaHCO_3$ to Na_2CO_3 may not occur to a significant extent so that only one mol of $NaHCO_3$ may react per mol of SO_2 at a low stoichiometry.
- The reactivity of $Ca(OH)_2$ with respect to dry SO_2 removal can be enhanced by slurrying lime with a silica source, such as flyash or diatomaceous earth, at elevated temperatures [85-95°C (180-200°F)] for prolonged periods (12-16 h).
- Slurrying flyash with $Ca(OH)_2$ at a weight ratio of 3:1 and injecting the resultant dry sorbent into humidified flue gas [Δt_s = 11-17°C (20-30°F)] resulted in an SO_2 removal of 50-80 percent over the SR range of 1-1.8, in the duct (0.8 s gas retention time)/baghouse system.
- Without product recycle, approximately 50 percent $Ca(OH)_2$ utilization occurred in the tests cited above. With product recycle the utilization increased to at least 70-80 percent at the same conditions.

- Tests using the same silica-enhanced sorbents injected into the duct (2.0 s gas retention time)/cyclone system without recycle at similar test conditions provided SO_2 removal efficiencies of only about 30 percent of those above.
- Introducing recycle of the sorbents by mixing the cyclone catch solids into the prepared slurry of silica-enhanced $Ca(OH)_2$ prior to duct injection avoided the need for separate drying/dewatering of the enhanced sorbent slurry; also, the overall $Ca(OH)_2$ utilization increased. The recycle solids also provided the silica for $Ca(OH)_2$ enhancement in lieu of flyash during slurrying at elevated temperatures.
- When using sorbent recycle, the duct injection/cyclone system (2.0 s gas retention time) resulted in SO_2 removals of about 50 percent at an SR of 1, and 50-90 percent at SRs in the range of 1 to 2.
- The results suggest that a dry injection process using silica-enhanced lime sorbents may be an attractive retrofit option for controlling SO_2 emissions from an existing coal-fired power plant equipped with an ESP.

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(3) R.N. Ruiz-Alsop: "Reaction of SO_2 with $Ca(OH)_2$," Ph.D. Dissertation, Department of Chemical Engineering, The University of Texas at Austin, 1986.

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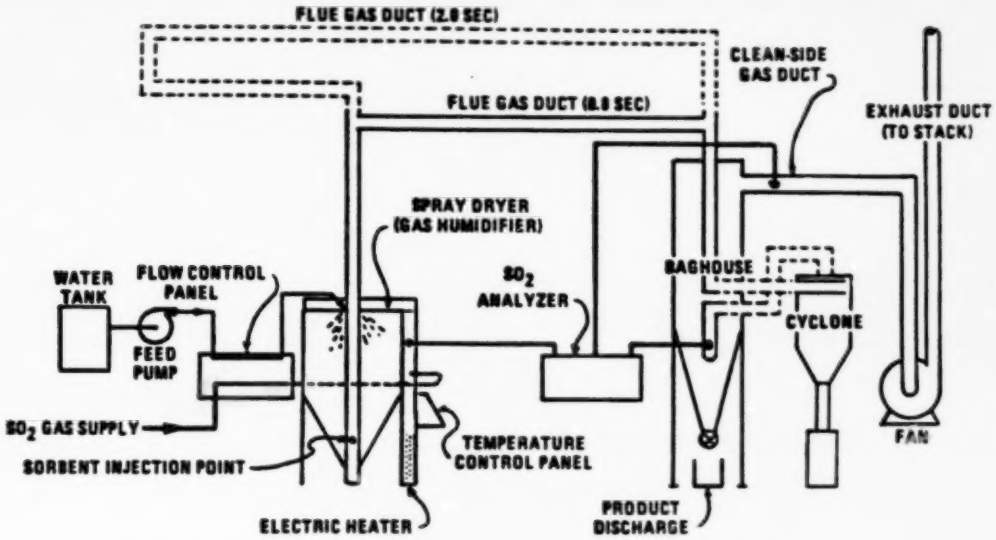

Figure 1. Schematic of duct injection pilot plant facility.

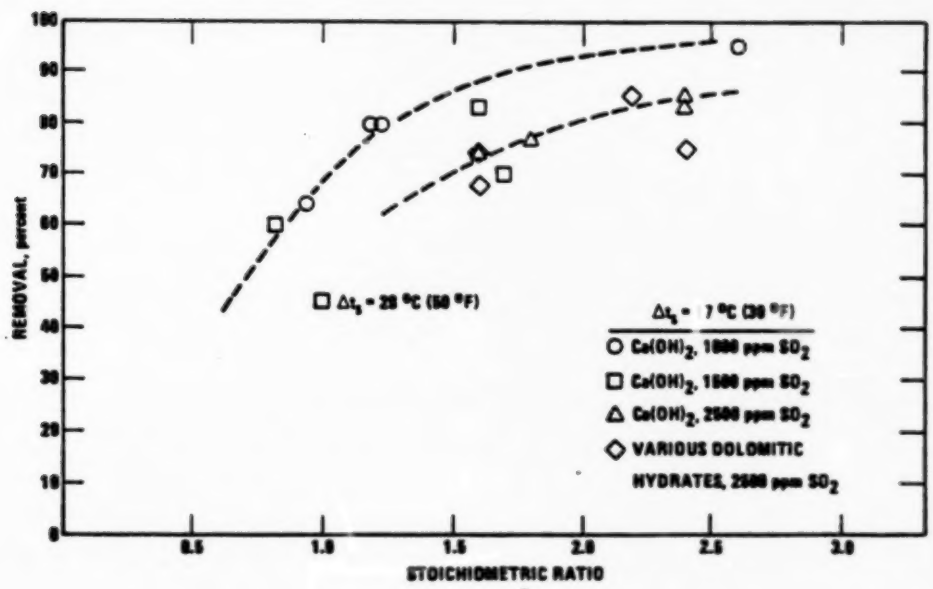

Figure 2. Removal of SO_2 in spray dryer/baghouse pilot plant facility with hydrated limes (calcitic and dolomitic) as sorbents.

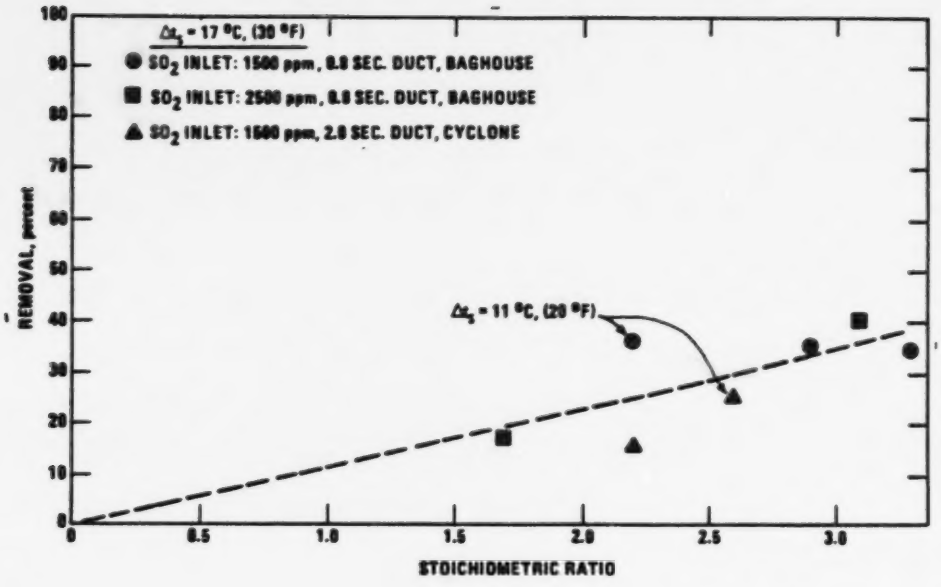
Δt_s = 17 °C, (30 °F)
SO_2 INLET: 1500 ppm, 0.8 SEC. DUCT, BAGHOUSE
SO_2 INLET: 2500 ppm, 0.8 SEC. DUCT, BAGHOUSE
SO_2 INLET: 1500 ppm, 2.8 SEC. DUCT, CYCLONE
Δt_s = 11 °C, (20 °F)
REMOVAL, percent
STOICHIOMETRIC RATIO

Figure 3. Removal of SO_2 by in-duct injection of hydrated lime in a pilot plant facility.

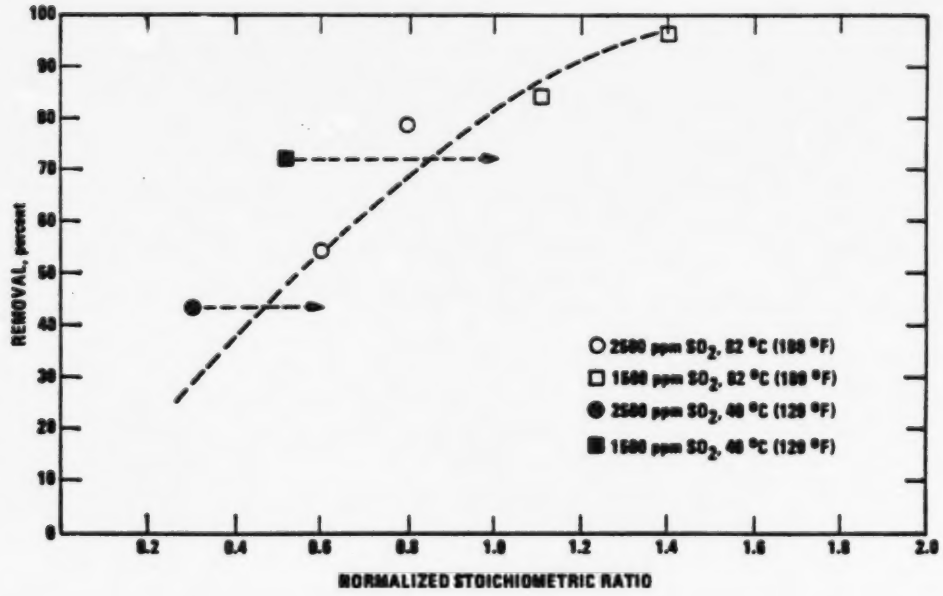
2500 ppm SO_2, 82 °C (180 °F)
1500 ppm SO_2, 82 °C (180 °F)
2500 ppm SO_2, 49 °C (120 °F)
1500 ppm SO_2, 49 °C (120 °F)
REMOVAL, percent
NORMALIZED STOICHIOMETRIC RATIO

Figure 4. Removal of SO_2 by a finely ground (10 μm) $NaHCO_3$ in a duct injection/baghouse pilot plant facility.

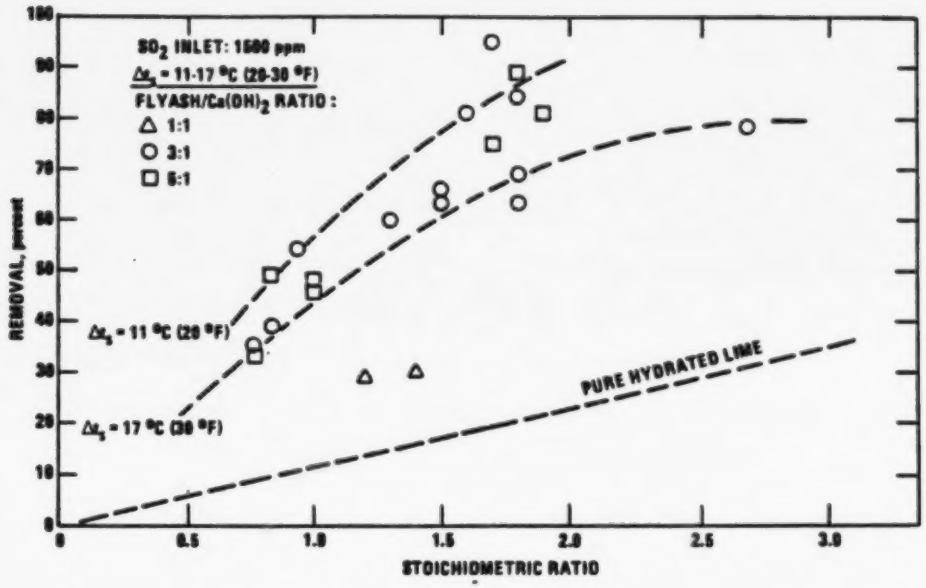

Figure 5. Removal of SO_2 with flyash-enhanced lime in a duct injection/baghouse pilot plant facility.

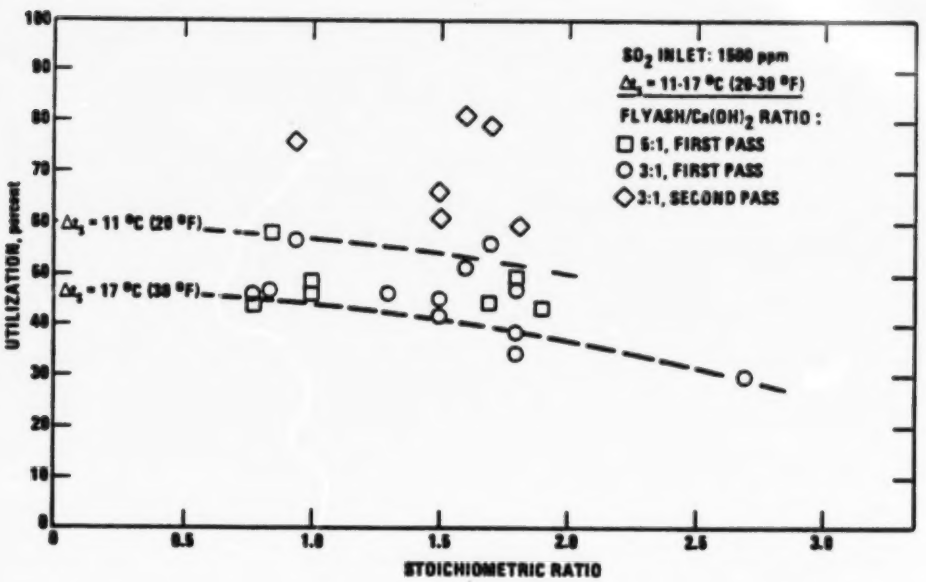
SO_2 INLET: 1500 ppm
Δt_s = 11-17 °C (20-30 °F)
FLYASH/$Ca(OH)_2$ RATIO :
5:1, FIRST PASS
3:1, FIRST PASS
3:1, SECOND PASS
Δt_s = 11 °C (20 °F)
Δt_s = 17 °C (30 °F)
UTILIZATION, percent
STOICHIOMETRIC RATIO

Figure 6. Calculated utilization of $Ca(OH)_2$ in flyash-enhanced lime. Duct injection/baghouse pilot plant facility.

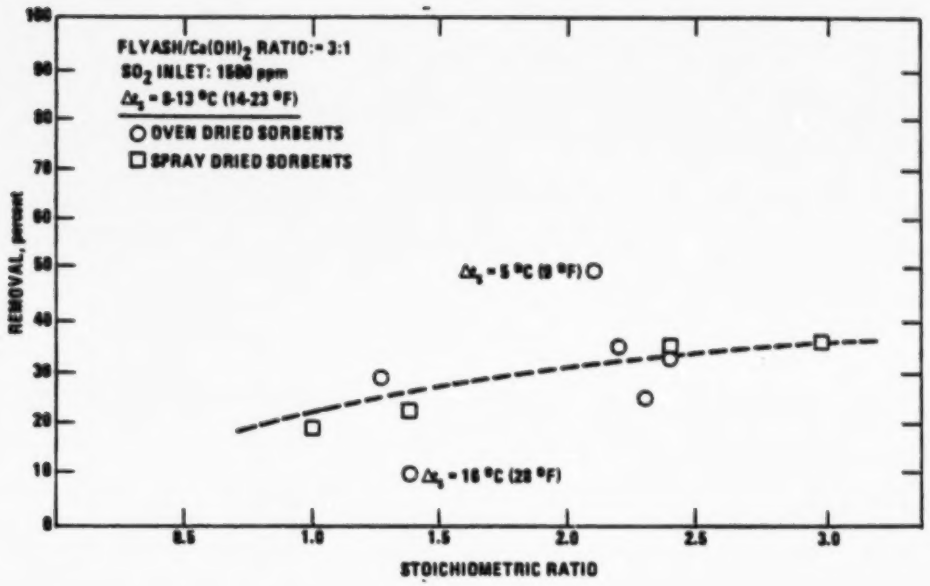
FLYASH/Ca(OH)2 RATIO: = 3:1
SO2 INLET: 1500 ppm
Δts = 8-13 °C (14-23 °F)
OVEN DRIED SORBENTS
SPRAY DRIED SORBENTS
Δts = 5 °C (9 °F)
Δts = 16 °C (28 °F)
REMOVAL, percent
STOICHIOMETRIC RATIO

Figure 7. Removal of SO_2 with flyash-enhanced lime in a duct injection/cyclone pilot plant facility (2.0 s gas retention time).

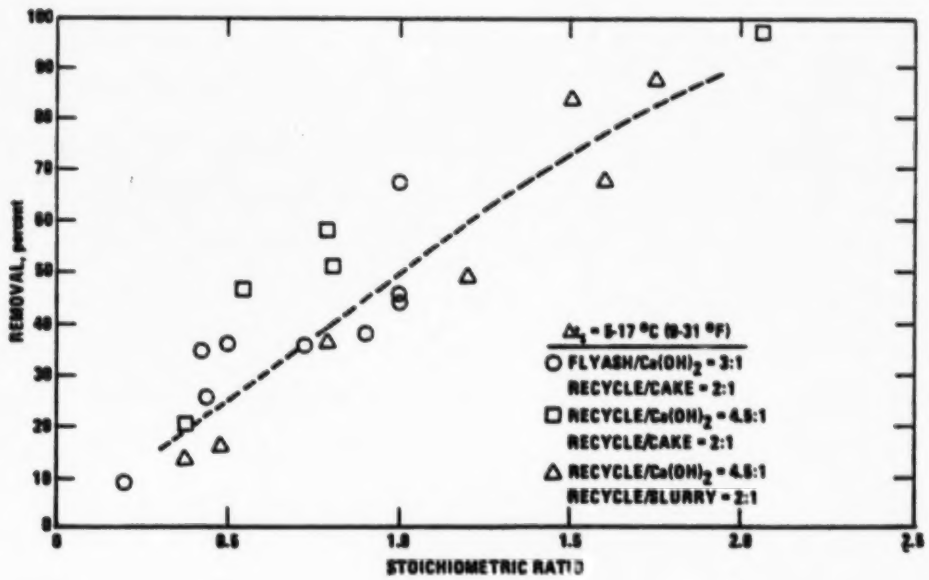

Figure 8. Removal of SO_2 in duct injection/cyclone pilot plant facility (2.0 s retention time); flyash-enhanced lime used as dry sorbent with recycle.

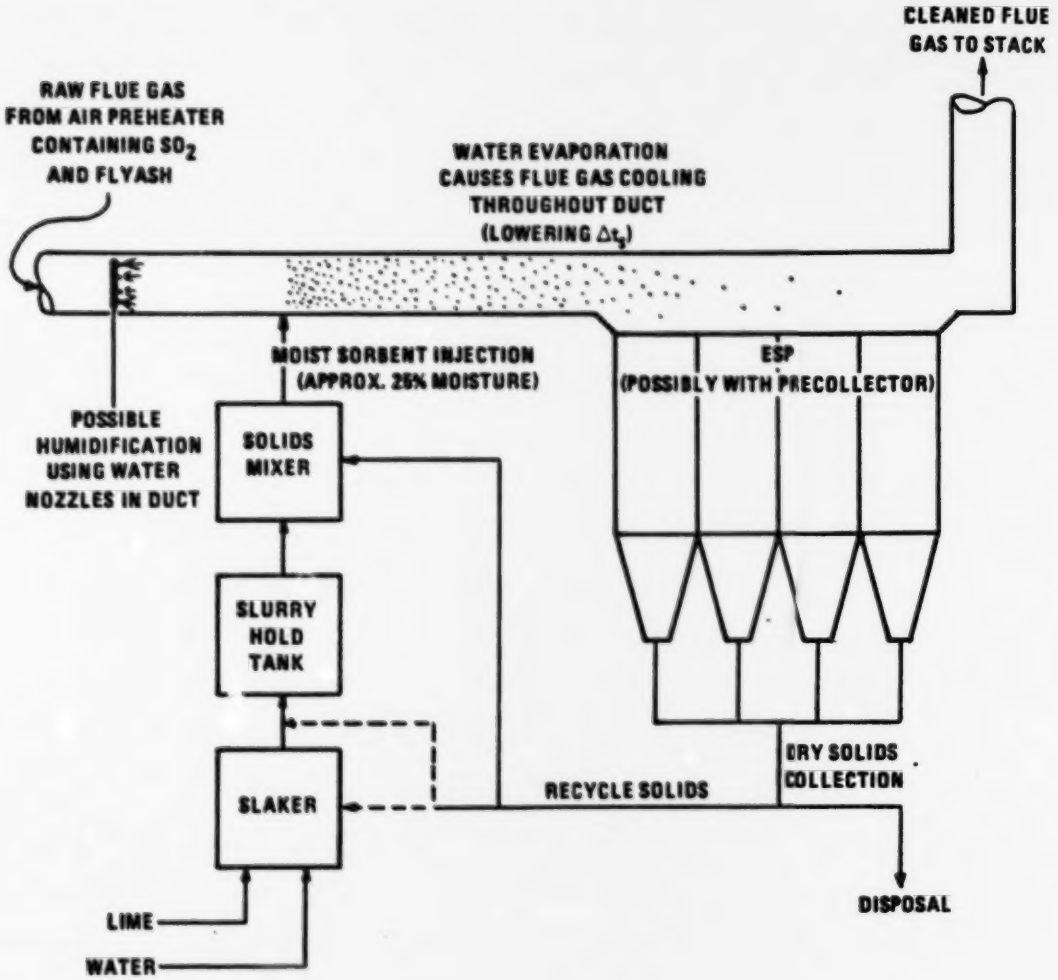
CLEANED FLUE GAS TO STACK
RAW FLUE GAS FROM AIR PREHEATER CONTAINING SO_2 AND FLYASH
WATER EVAPORATION CAUSES FLUE GAS COOLING THROUGHOUT DUCT (LOWERING Δt_s)
MOIST SORBENT INJECTION (APPROX. 25% MOISTURE)
ESP (POSSIBLY WITH PRECOLLECTOR)
POSSIBLE HUMIDIFICATION USING WATER NOZZLES IN DUCT
SOLIDS MIXER
SLURRY HOLD TANK
SLAKER
RECYCLE SOLIDS
DRY SOLIDS COLLECTION
DISPOSAL
LIME
WATER

Figure 9. Process flow diagram for a duct injection FGD system, using silica enhancement of lime and recycle.

TABLE 1. DRY INJECTION OF SODIUM BICARBONATE
Church and Dwight Grade 1 (Mean Particle Size 50-60 μm)

SO_2 inlet concentration, ppm	2500	2500	2500	2500	1500
Temperatures:					
Spray dryer inlet, °C(°F)	232(410)	204(400)	204(400)	177(350)	177(350)
Spray dryer outlet, °C(°F)	138(280)	93(200)	77(170)	49(120)	49(120)
Wet bulb, °C(°F)	41(106)	42(108)	42(108)	39(103)	39(103)
Baghouse outlet, °C(°F)	113(236)	78(173)	77(164)	50(122)	50(122)
ΔP baghouse, mm(in.) WG	45(1.8)	35(1.4)	48(1.9)	27(0.6)	28(1.1)
NSR*	2.5	2	2	1.9	1.9
SO_2 removal, %	68	54	48	34	59
Sorbent utilization**, %	27	27	24	18	31

$$*NSR = \frac{2 \times (\text{mol/h } NaHCO_3 \text{ injected})}{\text{mol/h } SO_2 \text{ injected}}$$

$$**\text{Utilization} = \frac{\text{mol/h } SO_2 \text{ removed}}{2 \times (\text{mol/h } NaHCO_3 \text{ injected})} = \frac{SO_2 \text{ removal}}{NSR}$$

TABLE 2. DRY INJECTION OF FLYASH-ENHANCED LIME SORBENT
Fresh Sorbent Cake Residual Moisture = 50-60%
Recycle Solids/Sorbent Cake = 1:1
Sorbent Mixture Oven Dried Prior to Injection
Duct Injection/Baghouse Pilot Plant Facility

Recycle test no.	1	2	3	4	5	6	7
Duration, h	7	7	6.5	7.5	6	7	7
SO_2 inlet concentration, ppm	1530	1550	1500	1480	1470	1450	1530
Temperatures:							
Spray dryer inlet, °C(°F)	177(350)	177(350)	176(349)	178(352)	180(356)	178(352)	179(355)
Spray dryer outlet, °C(°F)	49(120)	49(120)	49(120)	49(120)	50(122)	50(122)	50(122)
Wet bulb, °C(°F)	41(106)	41(105)	41(105)	41(105)	42(107)	41(106)	41(105)
Baghouse inlet, °C(°F)	49(121)	49(121)	51(123)	49(121)	51(123)	51(123)	49(121)
Baghouse outlet, °C(°F)	52(125)	52(126)	52(126)	52(125)	52(125)	52(125)	51(124)
ΔP baghouse, mm(in.) WG	78(3.1)	80(3.2)	78(3.1)	88(3.5)	78(3.1)	78(3.1)	68(2.7)
SR	0.59	0.62	0.53	0.61	0.62	0.62	0.53
SO_2 removal in duct, %	32	28	25	22	25	18	23
SO_2 removal in baghouse, %	36	33	28	31	25	31	22
SO_2 removal total, %	68	61	53	53	50	49	45
Utilization, %	115	98	100	87	81	79	85